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Published in:

Proceedings of the 1st International Symposium on Terahertz Nanoscience (TeraNano 2011) and 2nd Workshop of International Terahertz Research Network (GDR-I THz 2011)

Publication date:

2011

Document Version

Early version, also known as pre-print

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Citation (APA):

Cooke, D. G., Krebs, F. C., & Jepsen, P. U. (2011). Ultrabroadband time-resolved THz spectroscopy of polymer-based solar cells. In *Proceedings of the 1st International Symposium on Terahertz Nanoscience (TeraNano 2011) and 2nd Workshop of International Terahertz Research Network (GDR-I THz 2011)* <http://www.ile.osaka-u.ac.jp/research/THP/TeraNano/>

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Ultrabroadband time-resolved THz spectroscopy of polymer-based solar cells

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Abstract—We have developed ultrabroadband THz spectroscopy in reflection mode for characterization of conductivity dynamics in conductive polymer samples used in organic solar cells. The spectrometer is designed to have a time resolution limited only by the duration of the optical pump pulse, thus enabling the investigation of charge generation processes on the sub-100-fs time scale.

I. INTRODUCTION

Time-resolved THz spectroscopy is a very powerful tool for the investigation of ultrafast processes in condensed-matter systems [1]. It has been used for studies of carrier dynamics in a wide range of semiconducting materials, including bulk GaAs [2-3], thin films of crystalline, nanocrystalline, amorphous silicon [4], and TiO₂ [5] just to mention a few. Most studies to date have been focused on the region below 2 THz due to instrumentation limitations (electro-optic generation and detection in ZnTe crystals), and thus the nature of conductivity processes have partly been discussed on the basis of measurements of a small section of the full conductivity spectrum. Larger bandwidth measurements have proven their value in several investigations, as exemplified by references [6-8].

Here we demonstrate a time-resolved THz spectroscopy (TRTS) system which employs air plasma generation of ultrashort THz pulses [9-10] in combination with air biased coherent detection (ABCD) of the THz transients [11].

Figure 1 shows a schematic diagram of the experimental setup.

The generation and detection processes are both based on four-wave mixing in air. As in any other frequency conversion processes, the bandwidth of the process is always limited by the bandwidth of the laser source and the bandwidth of the phase matching. With air as the nonlinear medium the phase matching conditions are perfect over an extremely broad bandwidth range, and therefore the bandwidth of the generation and detection processes is in practice limited only by the laser bandwidth.

We use a transform-limited 35-fs laser pulse from a standard regenerative amplifier system (SpectraPhysics Spitfire),

resulting in THz transients with a spectral coverage from 1 to 35 THz and a THz pulse duration of less than 50 fs.

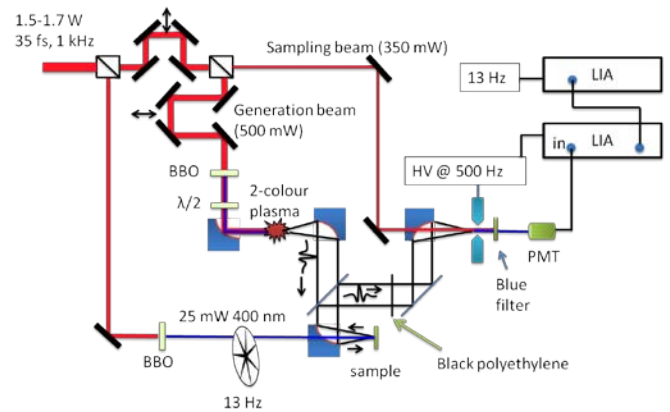


Figure 1: Schematic diagram of ultrabroadband time-resolved THz spectroscopy setup operating in normal-incidence reflection mode.

With this system we perform optical pump – THz probe spectroscopy of the evolution of the photoinduced conductivity in a roll-to-roll processed, device-ready bulk heterojunction film consisting of a blend of the conductive polymer P3HT (electron donor) and PCBM (electron acceptor) [12]. Figure 2 shows the chemical structure of P3HT and PCBM.

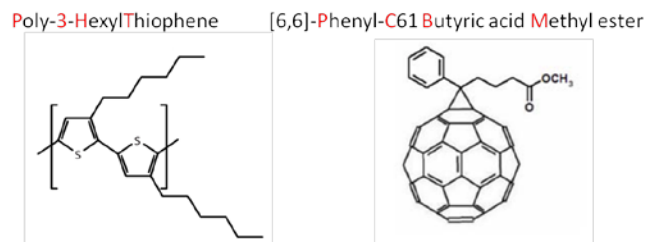


Figure 2: Chemical structure of P3HT and PCBM

The pump-probe spectroscopy is carried out with a 400-nm pump pulse (< 40 fs duration) exciting the sample at a time $\Delta\tau$ before reflection of the THz pulse. The photoinduced changes of the conductivity leads to modifications of the reflection amplitude and phase of the THz signal,

$$1 + \frac{\Delta E(\omega, \Delta\tau)}{E_{ref}(\omega)} = \frac{1 - n - Z_0 d \sigma(\omega, \Delta\tau)}{1 + n + Z_0 d \sigma(\omega, \Delta\tau)} \frac{1 + n}{1 - n} \quad (1)$$

where n is the index of refraction of the substrate, Z_0 is the free-space impedance, d is the sample thickness, and $\sigma(\omega, \Delta\tau)$ is the frequency-dependent, complex-valued photoconductivity at the pump-probe delay time.

Figure 3 shows an example of the evolution of the conductivity of the P3HT/PCBM device-ready thin film subsequent to photoexcitation [13].

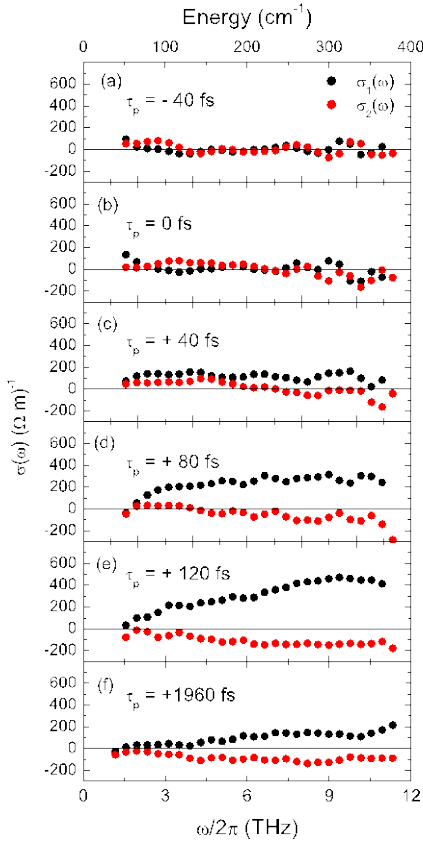


Figure 3: Short time evolution of the real (black circles) and imaginary (red circles) part of the conductivity of the P3HT/PCBM BHI film after 400-nm photoexcitation.

Initially the conductivity spectrum displays a Drude-like response, indicating mobile charges. Later, the suppression of the DC conductivity and the negative sign of the imaginary part of the conductivity show a more localized response.

ACKNOWLEDGMENTS

David Cooke acknowledges financial support from NSERC and the H. C. Ørsted Fund.

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